Synthesis and Application of Imogolite Nanotubes

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Introduction

Imogolite (IMO) is a naturally occurring aluminosilicate nanotube that can also be produced synthetically through a solution-phase, low temperature procedure.

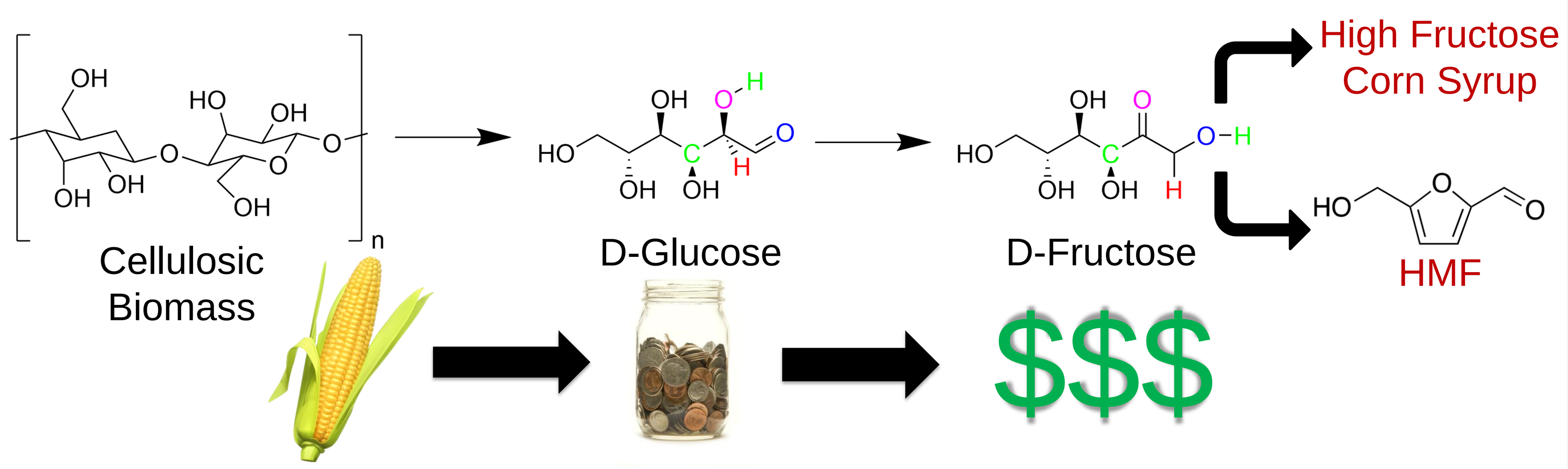
Fig. 1: Imogolite in its natural mineral form.[1]

- Empirical formula: $(OH)_3Al_2O_3SiOH$
- Outer Diameter = 2 nm
- Length = 100 nm
- Synthesized with monodisperse, tunable dimensions and compositions
- Present an innovative shape-selective catalytic platform: **Glucose to fructose isomerization**
- Tune structure and properties through rational changes to the synthesis
  - Integration of heteroatoms

Motivation

Rising energy costs and concerns regarding climate change necessitate the development of an alternative and sustainable fuel source to replace petroleum-based fuels.

- Biomass: most abundant raw material/carbon source on the planet; current conversion methods suffer from low conversion and/or low selectivity
- Glucose to fructose isomerization: a key step in the conversion of biomass into useful fuels and chemicals that could benefit from an improved catalyst[2]
- Heterogeneous catalysts: provide a means to improve yield and selectivity of selected products, thus aiding in creation of sustainable production processes



Approach

- Begin with synthesis of pure imogolite nanotubes as basis for comparison
- Mix starting materials in a N_2-filled glovebox
- Molar ratio: 1:2:1 Si:Al:$HClO_4$
- Hydrothermal aging in acidic conditions
- Dry and grind into a fine powder or keep as dialyzed gel

Post-synthesis:

- Characterize the materials completely using X-ray diffraction, nitrogen physisorption, and thermogravimetric analysis
- Perform catalytic testing to determine the activity for the isomerization of glucose to fructose

- Synthesize hybrid IMO by using a similarly-structured precursor containing Ge, Sn, Ti, Zr, Hf
- Low substitution: prevent disruption of requisite curvature

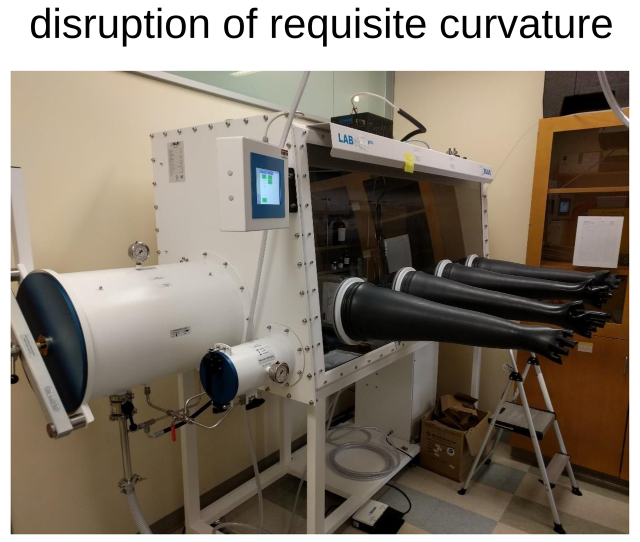


Fig. 2: Glovebox used in the synthesis.

Project Goals

1. Synthesize and characterize pure imogolite to provide baseline for comparison with hybrid material.
2. Introduce heteroatoms (Ge, Sn, Ti, Zr, Hf) into the structure and characterize the hybrid imogolite.
3. Perform tests of catalytic activity for the isomerization of glucose to fructose

Inspiration

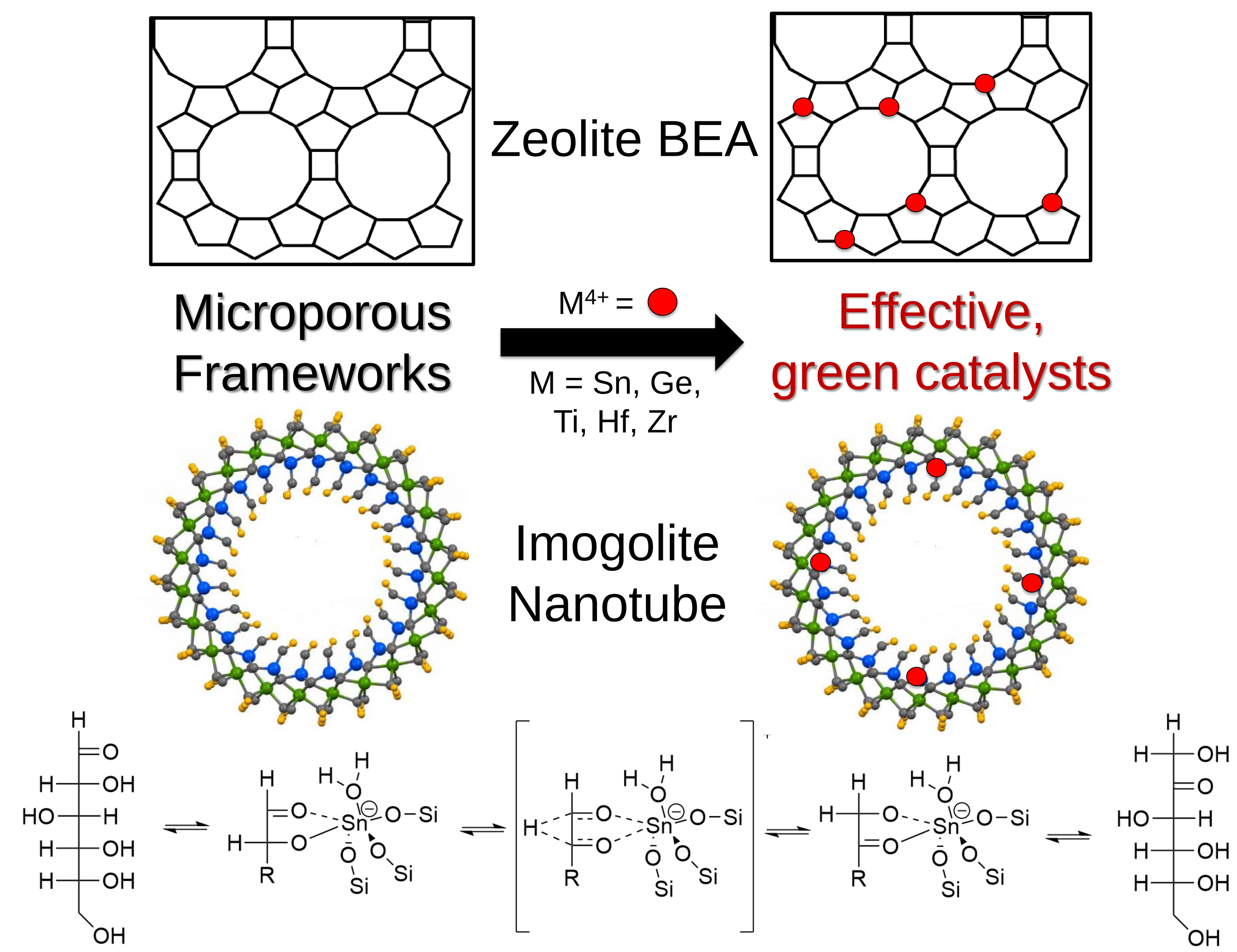


Fig 3: Glucose to fructose isomerization catalyzed by Sn-BEA.

Results: Material Synthesis

- Pure IMO successfully synthesized via a known procedure
- Macroscopically appears as flakes after drying

Fig 4: Pure imogolite after drying (left) and grinding (right).

Results: X-Ray Diffraction

- X-ray diffraction (XRD) provides insight on the atomic structure of the nanotubes through distinct diffraction patterns
- Utilize XRD as a tool for comparison: compare pure IMO against literature patterns and hybrid IMO against pure material

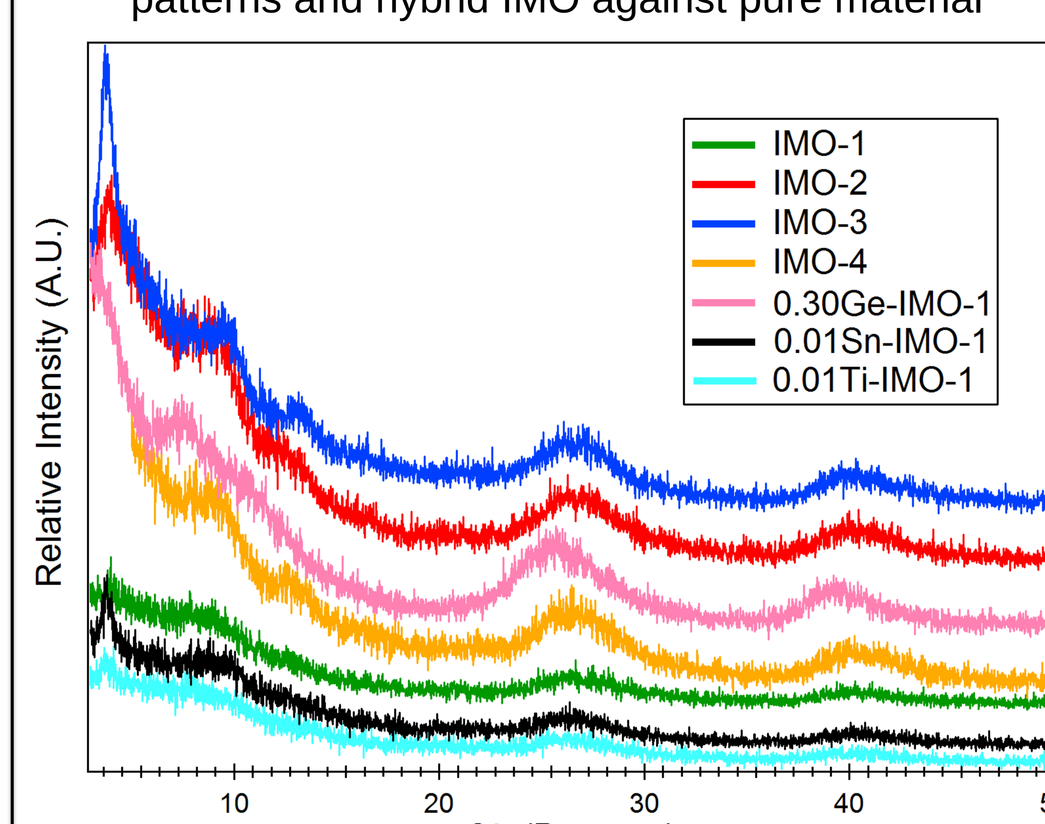


Fig. 5: XRD patterns for synthesized IMO.

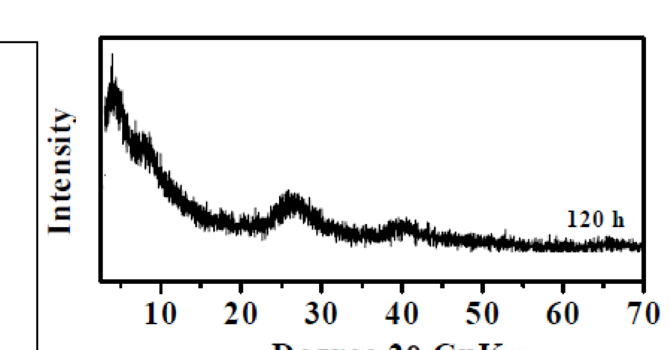


Fig. 6: XRD pattern from literature for pure imogolite.[4]

- Diffraction pattern for most of the synthesized materials matches accepted pattern from literature

Results: N_2 Physisorption

- Nitrogen physisorption uses nitrogen gas, cryogenic temperatures, and adsorption to elucidate the porous nature of the nanotubes
- Determine surface area, pore volume, and pore diameter from adsorption isotherms

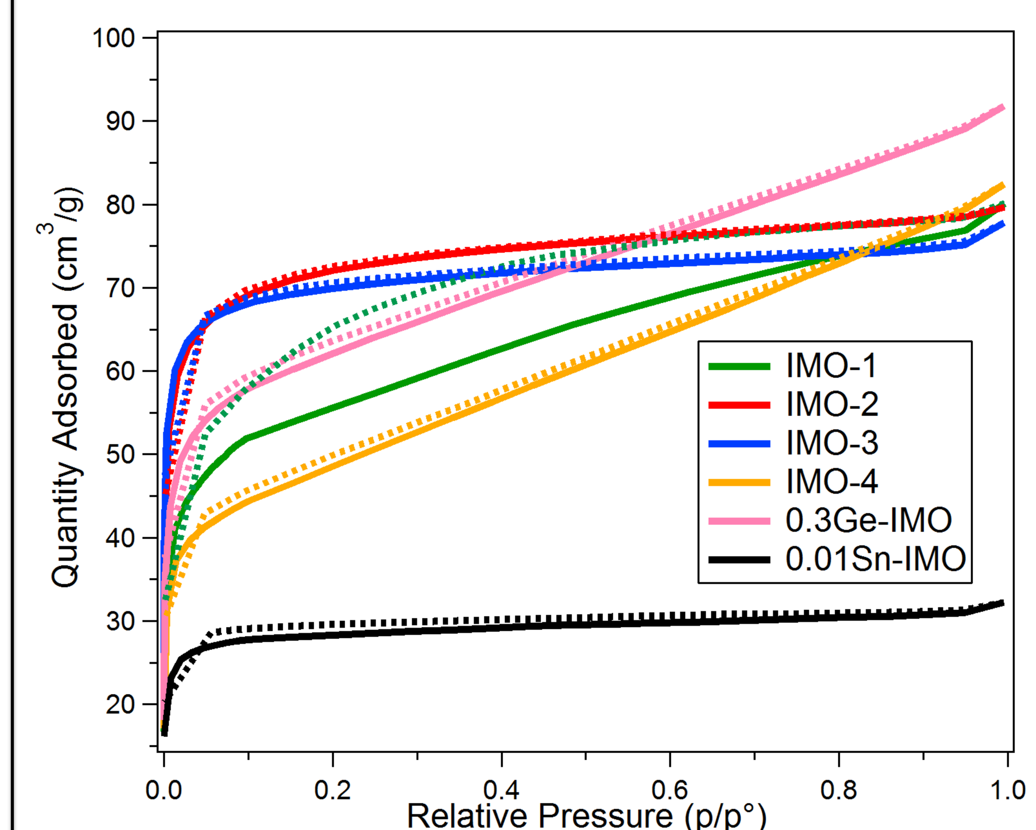


Fig 7: N_2 physisorption isotherms for synthesized IMO.

Step 1: Determine isotherm type

- Type I(b) – Microporous, <2.5 nm
- Indicated by sharp rise under 0.1 relative pressure
- Result of enhanced adsorbent-adsorptive interactions in narrow micropores[5]

Step 2: Apply computational procedures to determine surface area and pore width

- BET Method: calculates total surface area
- For pure IMO, values range from 250 – 400 m^2/g
- HK Method: calculates pore width for micropores
- For pure IMO, values range from 0.8 – 1.2 nm

Sample	S_{BET} (m^2/g)	Pore Width (nm)
IMO-1*	207	1.0
IMO-2	274	1.0
IMO-3	273	0.9
IMO-4	178	0.9
0.01Sn-IMO-1	110	1.0
0.30Ge-IMO-1	229	0.9

Fig 8: Results for surface area and pore width.

Conclusions

- Pure imogolite successfully synthesized and characterized: provides baseline
- Pure IMO-2, 3, 4 and Ge-substituted batches determined to have been successful
- Pure IMO-1, Sn- and Ti-substituted batches require further analysis
- Degas temperature critical for nitrogen physisorption analysis

Future Work

- Determine a conclusive method to confirm if substitution was successful
- Syntheses using Zr and Hf precursors
- Perform catalytic testing on synthesized materials for the isomerization reaction
- Metallic nanoparticles: synthesis and immobilization
- Further investigation of potential catalytic reactions

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